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Acid mine drainage treatment with dunite

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ABSTRACT

This paper reports the efficiency of dunite as an alternative alkalinity generating material and adsorbent for the passive treatment of acid mine drainage (AMD). The acid neutralization capacity (ANC) of dunite has been investigated by contacting dunite (powder) samples with laboratory (acidic) solution and AMD samples and it has been shown that the ANC of dunite is 1 mmol/g dunite and is basically ascribed to the MgO content of the rock material. On the other hand contacting 1 g/l and 10 g/l dunite with AMD samples, results in increasing pH and significant removal of various metal ions (e.g. Cr(III), Co(II), Ni(xII), Pb(II)) contained in AMD. The latter is basically attributed to the precipitation of metal ions due to the pH increase in the AMD solutions.

Keywords: AMD; Dunite; Acid-base properties; Heavy metals; Removal

1. Introduction

Acid mine drainage (AMD) forms when sulfide minerals in rocks are exposed to oxidizing conditions in coal and metal mining, highway construction and other large-scale excavations. There are many types of sulfide minerals, but iron sulfides, pyrite and marcasite (FeS2), are the predominant AMD producers. Upon exposure to water and oxygen, pyritic minerals oxidize to form acidic, iron and sulfate-rich drainage. Specifically, pyrite oxidation creates sulfuric acid and ferrous and ferric sulfates, the corresponding reactions can occur spontaneously or can be catalyzed by microorganisms that derive energy from the oxidation reaction. The reactions, which describe the pyrite oxidation to form sulfuric acid and ferric hydroxide are the following:

$$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (1)$$

The oxidation of the sulfide to sulfate solubilizes the ferrous iron (Fe(II)), which is subsequently oxidized to ferric iron (Fe(III)).

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (2)$$

Ferric iron is partially hydrolysed releasing hydrogen ions (H^+)

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

or oxidizes additional pyrite

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

AMD can have severe impacts to aquatic resources, can stunt terrestrial plant growth, contaminate groundwater and raise water treatment costs [1,2]. Considerable effort has been expended in investigating the neutralization of AMD, because the main environmental concerns are associated with the acidity of the effluents [3]. A number of factors dictate the level of sophistication of the treatment system that is necessary to ensure that effluent standards will be met. These factors include: chemical characteristics of the AMD, the quantity to be treated, climate, terrain, sludge characteristics and projected life of the facility. The chemicals usually used for AMD treatment include limestone, hydrated lime, soda ash, caustic soda and ammonia [4,5]. Each chemical has

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characteristics that make it more or less appropriate for a specific condition and the best choice among alternatives depends on both technical and economic factors [6–11].

In Cyprus, abandoned pyrite mines are one of the most significant contributors to water contamination and potential sources of large-scale environmental pollution. On the other hand in arid and semi-arid areas (e.g. Cyprus), even AMD after proper treatment could be useful as an irrigation water resource. Hence, the investigation of locally available and low cost materials for the neutralization and removal of metal ions from AMD is of particular interest. In this study we have investigated the acid neutralization and sorption properties of dunite for its potential use in the AMD treatment [12]. Dunite is the olivine-rich end member of the peridotite group of mantle-derived rocks. The rock material (dunite) used in this study originated from a mountainous area of Cyprus [13].

The objectives of this study were (1) to determine the acid neutralization capacity of dunite and the origin of its alkaline properties and (2) to investigate the effectiveness of acid mine drainage treatment by dunite, with special emphasis on metal ion removal.

2. Materials and methods

2.1. Dunite

Dunite used in this study originated from a mountainous area of Cyprus (Troodos massif). Prior to application the material was sieved and the particle fraction of 80 mesh was selected for the adsorption experiments and was used without any further purification or other pre-treatment. The surface area of the adsorbent (granulated material) was measured by N_2-adsorption (Micromeritics Co, ASAP 2000) based on the BET equation published by Brunauer, Emmet and Teller [14]. It has been shown that dunite has a small internal surface (5.7 m^2/g), indicating that adsorption of metal ions and other contaminants occurs on its external surface. Further characterization of the material was done using FTIR (8000 Series, Shimadzu), XRD (6000, Shimadzu) and XRF (Spectrace, Shimadzu) [12].

2.2. Dunite interaction with acidic solutions

Dunite powder samples of various amount (0.1, 1 and 10 g) were added to 1 liter de-ionized water, and either 1 liter of 0.001c $HClO_4$, 0.01 M $HClO_4$ or 0.1 M $HClO_4$ solutions. The suspensions were regularly stirred and the pH in solution was measured as a function of time. After stabilization of the pH the solid phase (dunite) was removed by centrifugation and investigated by SEM-EDX (Vega TS5136LS/Tescan).

2.3. AMD Treatment with Dunite

AMD samples obtained from lagoons corresponding to two different pyrite mines found in Cyprus, were placed in contact with different amounts of dunite (1, 10, 100, 250 and 500 g/l) and the equilibrium pH in solution was determined as a function of time. The pH value was stabilized after 7 days time of contact. Furthermore, for the suspensions of 1 and 10 g dunite/l AMD the concentration of boron and various metal ions (e.g. Cr, Co, Ni, Pb) was determined in solution by ICP-OES (Shimadzu).

3. Results and discussion

3.1. Dunite interaction with acidic solutions

Figure 1 shows the equilibrium pH, that is established after addition of dunite to de-ionized water and aqueous $HClO_4$ of different concentration. According to figure 1, addition of three different amounts of dunite (0.1, 1 and 10 g/l) to de-ionized water results in increasing pH to 6.8, 7.7 and 9.1, respectively, indicating the alkaline character of the rock material (dunite). On the other hand, addition of 0.1 g dunite in the acidic solutions had little affect the pH in the respective solutions, because the amount of dunite added is far below than the amount needed for the neutralization of the acid in solution.

Addition of 1 g/l dunite in the acidic solutions results in almost quantitative neutralization of the 0.001 M $HClO_4$ solution and allows estimation of the acid neutralization capacity of dunite, which is calculated to be 1 mmol equivalents per gram dunite. However, the pH of the solutions with higher acid concentration (e.g. 0.01 and 0.1 M $HClO_4$) remains almost constant, indicating that 1 g/l dunite is far below the amount of dunite needed for the quantitative neutralization of these solutions. As expected from the previous results, 10 g/l dunite is far above the amount needed for the neutralization of the 0.001 M $HClO_4$ solution and enough to almost neutralize the 0.01 M $HClO_4$ solution, validating the value of the acid neutralization capacity of dunite, estimated from the previous experiment (1 mmol/g dunite). Nevertheless, the pH of the 0.1 M $HClO_4$ sample remains unaffected even after the addition of 10 g/l dunite to the solution.

The alkalinity of dunite originates from basic oxides/hydroxides included in the rock and particularly MgO/$Mg(OH)_2$. According to figure 2, which shows SEM-EDX spectra of dunite samples treated with pure water and aqueous $HClO_4$ solutions of different concentration (A: pure water; B: 0.01 M $HClO_4$; C: 0.1 M $HClO_4$) increasing acid concentration in solution results in the relative reduction of the Mg peak in the spectra and

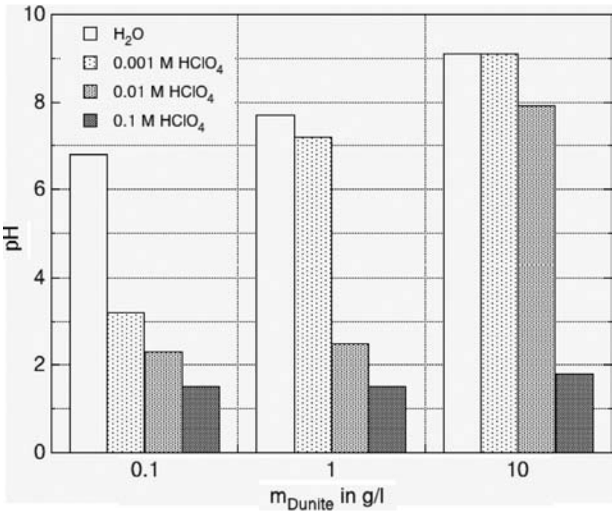

Fig. 1. Equilibrium pH established in de-ionized water and aqueous $HClO_4$ solutions of different concentration after addition of dunite.

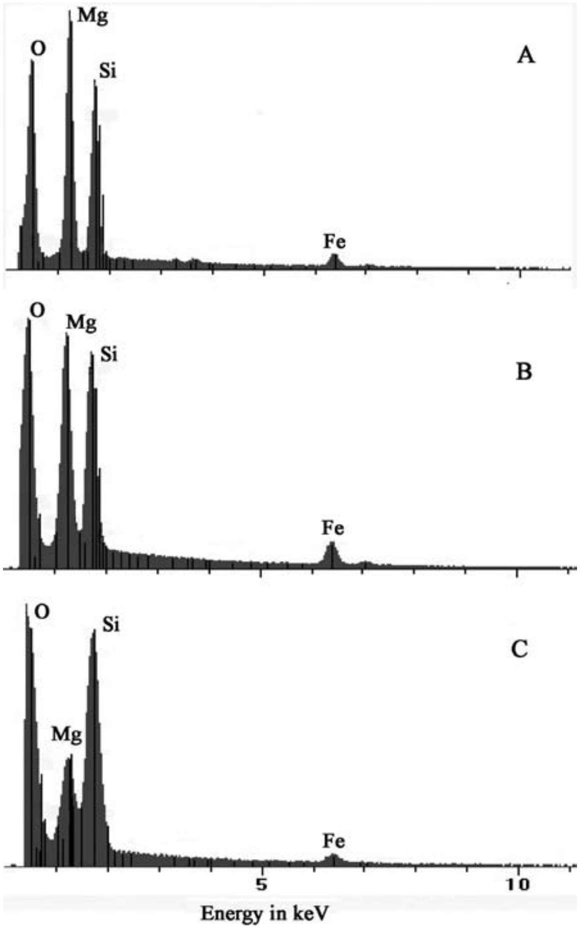

Fig. 2. SEM-EDX spectra of dunite samples after treatement with aqueous $HClO_4$ solutions of different concentration (A: pure water; B: 0.01 M $HClO_4$; C: 0.1 M $HClO_4$).

hence in the reduction of Mg in the corresponding samples, indicating clearly that the alkalinity of the dunite originates from "MgO" content of the rock material. According to ED-XRF measurements the "MgO" content of the dunite used here is about 4%. The neutralization reaction that leads to the pH increase of the acidic solutions is given by following equation.

$$MgO + 2H^{+} \rightarrow Mg^{2+} + H_2O \tag{5}$$

and

$$Mg(OH)_2 + 2H^{+} \rightarrow Mg^{2+} + 2H_2O \tag{6}$$

The acid-base neutralization reaction increases the pH of the solution due to the consumption of hydrogen ions and leads to dissolution and removal of Mg^{2+} ions from the surface. The latter explains the relative reduction of the Mg peak in the spectra of the dunite samples treated by acidic solutions.

3.2. AMD treatment with dunite

Figure 3 shows the equilibrium pH after addition of different amounts of dunite to 1 liter of AMD from two different pyrite mine lagoons found in Cyprus. The initial pH of the AMD samples is pH 2.75±0.05 and corresponds approximately to an acidic solution of 0.001 M $HClO_4$ solution. However, in contrast to the previous experiments the addition of even 100 g/l of dunite is not enough to quantitatively neutralize the acidic solution. This is ascribed to the fact that the dunite alkalinity is mainly consumed by the hydrolysis reactions of the polyvalent metal ions (e.g. Fe(III), Cr(III)) contained in the AMD solutions, which start at very low pH. Hence

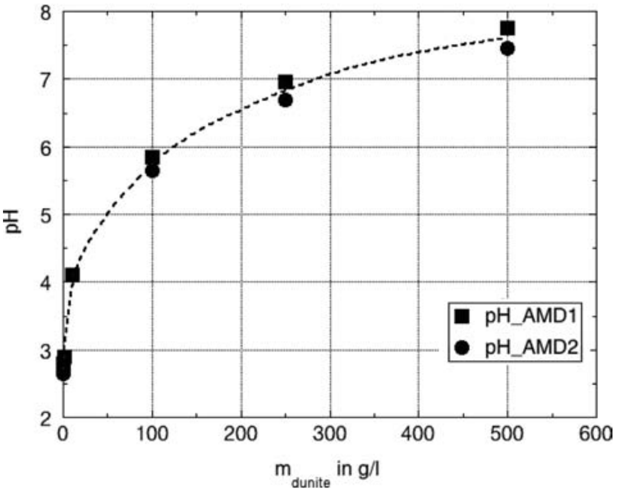

Fig. 3. pH of two different AMD solutions after addition of different amounts of dunite.

the removal of the metal ions from AMD is basically due to (co)precipitation reactions [15,16].

The metal ion concentration before and after treatment of the AMD solutions with two different amounts of dunite (e.g. 1 and 10 g/l) is summarized in Table 1. The relative removal of the metal ions from the AMD solutions after treatment is shown graphically in figure 4. According to figure 4 the highest removal efficiencies for both AMD solutions are observed for boron, iron cobalt, nickel and lead. Because of both effects, the pH enhancement and the removal of metal ions, treatment of acidic wastewaters (e.g. AMD, industrial effluents) with dunite could be applied as a first step in water treatment technologies, which require increased pH and relatively low metal ion concentration [17,18]. Generally, increasing the amount of dunite affects positively the metal ion removal from AMD. However, this is not the case for chromium and nickel ions (indicated by the circles in figure 4). Increasing the amount of dunite from 1 g/l to 10 g/l results in decreasing removal efficiency of about 60% and 10% for nickel and chromium, respectively. Taking into account that increasing the amount of dunite affects basically the pH of the AMD solution and hence (co)precipitation and adsorption processes, the previously mentioned effect could be attributed to competition reactions between Cr(III) and Fe(III), and Ni(II) and Cu(II) or Pb(II). The data in Figure 4 (Table 1) show clearly that the removal efficiency of the "competitor" metal ions (under the given conditions) increases significantly with increasing dunite amount, supporting the above assumption.

Table 1
Metal ion concentration prior to and after the treatment of the AMD solutions with two different amounts of dunite (e.g. 1 and 10 g/l).

Species (mg/l)	AMD1			AMD2		
	Prior treatment	After treat. (1 g/l)	After treat. (10 g/l)	Prior to treatment	After treat. (1 g/l)	After treat. (10 g/l)
B	2.1	0.9	0.5	1.8	1.0	0.9
Cr	10.4	1.3	2.3	10.3	1.1	2.2
Mn	111.2	100.7	76.9	104.9	94.9	79.8
Fe	306.7	214.0	14.2	315.8	217.9	156.8
Co	21.5	6.1	7.2	18.9	3.1	1.7
Ni	6.4	1.2	5.2	6.2	1.2	4.0
Cu	28.0	18.8	11.9	78.0	71.9	39.8
Zn	39.3	35.7	33.3	193.6	171.4	141.6
Pb	5.1	3.7	2.2	5.7	1.9	0.1

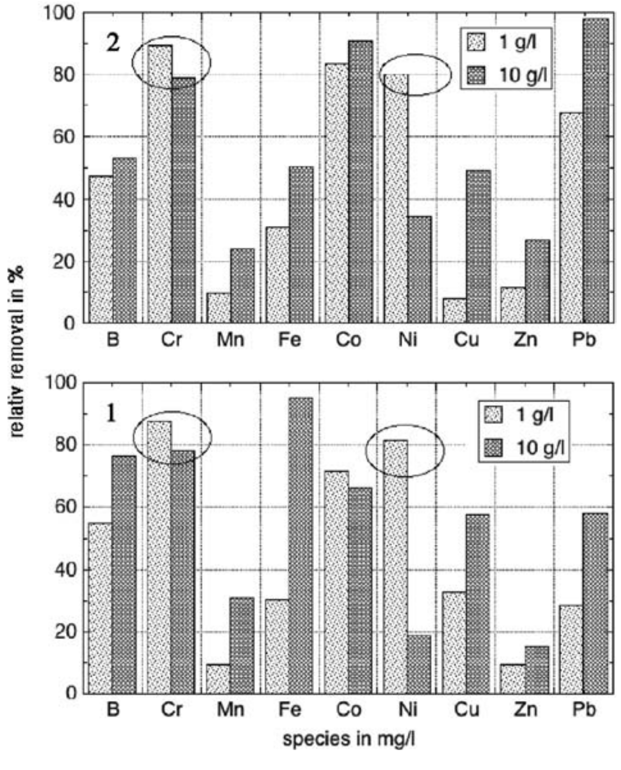

Fig. 4. Relative removal of metal ions from two different AMD solutions (1 and 2) treated with 1 g/l and 10 g/l dunite.

4. Conclusions

The results obtained from this study lead to the following conclusions:

1. The ANC of dunite is 1 mmol/g and is basically attributed to the MgO content of the material.
2. Addition of 1, 10, 100, 250 and 500 g dunite to 1 liter AMD (pH 2.8) increases the pH of the AMD solution to pH 2.9, 4.1, 5.7, 6.7 and 7.8, respectively.
3. Treatment of 1 liter AMD with 1 g and 10 g results in significant removal of various metal ions (e.g. Cr, Co,

Ni, Pb) from solution basically by precipitation due the hydrolysis of the respective metal ions.

4. Dunite could be used as low-cost material for AMD treatment in Cyprus and elsewhere if naturally available.

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